HIGH TEMPERATURE PROTECTIVE

COATINGS FOR REFRACTORY METALS

by

J. Rexer

PROGRESS REPORT NO. 7

Prepared Under Contract No. NASw-1405

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION
PARMA, OHIO

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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I. INTRODUCTION

The research, performed under Contract NASw-1405, is a continuation of work initiated under Contract NASw-1030.[1] The major objectives of the present program are 1) to measure the change in thickness of an iridium coating on the refractory metals tungsten, molybdenum, and niobium annealed at several temperatures for various times and 2) to examine the mechanical behavior of iridium-coated and heat-treated specimens with a microbend tester.

This report summarizes the research effort for the period 21 October 1967 to 21 January 1968. Complete descriptions of the materials used, methods of sample preparation, and apparatus were given in previous quarterly reports.

II. SUMMARY

The two molybdenum-iridium diffusion couples previously hot-pressed were sectioned. Microscopic examination of the molybdenum-iridium interfaces did not reveal intermetallic compound formation. A strip from each hot-pressed couple was bent in flexure with the microbend tester. The bending strength of the composites was higher than the strength of heat-treated, uncoated, molybdenum. Cracks initiated in the composite during bending at the outer iridium surface and propagated through the iridium towards the molybdenum-iridium interface.

Additional sections of the hot-pressed couples were metallographically polished on one surface, and the thickness of the iridium coating measured microscopically. The specimens were then annealed and remeasured to determine the loss of iridium as a function of time and temperature.

III. PROGRESS

A. Mechanical Behavior of Iridium-Molybdenum Composites

Several strips approximately 1/8-inch wide by 3/4-inch long were sectioned from the molybdenum-iridium composites previously prepared by hot-pressing 0.005-inch thick iridium and 0.020-inch thick molybdenum sheets together at approximately 1100°C and 2700 psi for 1-1/2 hours. The strips were metallographically polished on a 3/4-inch long side showing both substrate and coating. Microscopic examination of the molybdenum-iridium interfaces did not reveal intermetallic compound formation. A strip from two hot-pressed couples was tested with the microbend tester with the outer iridium edge at maximum tension and the outer molybdenum edge under a compressive force. In both samples, cracks started at the outer iridium edge and propagated in an irregular path towards the molybdenum-iridium interface. No observations could be made as to whether the crack propagated along the iridium grain boundaries or across the grains since the samples were not etched. Etching to reveal the iridium microstructure would involve severe chemical attack of both the molybdenum substrate and the interface. The initial cracks were observed at an applied load of 8-1/2 lbs for sample 6 M-B and nine lbs for sample 7 M-B. These loads correspond to strength of 1.01 x 10^{-5} psi and 1.04 x 10^{-5}psi, respectively. Additional data are given in Table I. Both samples were bent to approximately 45 degrees and failed suddenly when a crack reached the molybdenum-iridium interface.

TABLE I

Flexural Test Results for Hot-Pressed Molybdenum-Iridium Couples

Sample* Number	Width, B, Inches	Thickness, D, Inches	Maximum Applied Load, P, Lbs.	Flexural** Strength psi x 10^5
6M-B	0.1207	0.0256	12	1.42
7M-B	0.1161	0.0264	13	1.51

* Both samples were tested with a fixture having a 0.625-inch span, L, and three-point loading.

** Calculated using the expression: $S = \frac{3/2\ PL}{BD^2}$.

No delamination of the coating from the substrate was observed until one or more cracks reached the interface. Then in a very rapid sequence, (the total time lapse was approximately one second) a crack widened, the leading crack tip propagated a very short distance along the interface, and the molybdenum failed.

Uncoated molybdenum subjected to the same tests did not fracture; however, the applied load reached a maximum and then decreased as bending was continued. The maximum strengths ranged from 1.70×10^5 psi to 2.08×10^5 psi in the as received condition, and 1.04×10^5 psi when heat treated at 1550°C for one hour. These results were given in the previous progress report. A comparison of the mechanical behavior of uncoated and iridium coated molybdenum indicates that there is no decrease in the total bending strength due to the coating and diffusion bond obtained on hot-pressing. Nevertheless, uncoated molybdenum was ductile and did not fracture; the coated molybdenum fractured in a brittle manner after the coating failed and the composite was bent to approximately 45 degrees. Figure 1 is a macrophotograph of a coated molybdenum specimen after testing.

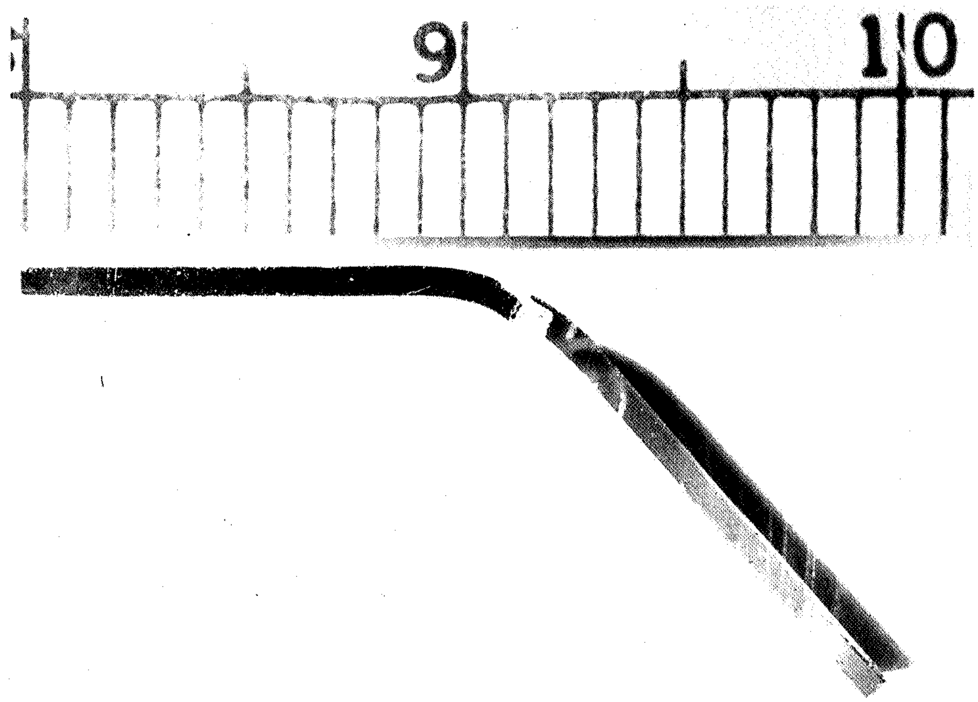

Figure 1. Macrophotograph of a Bent Test Sample of Hot-Pressed Molybdenum-Iridium

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B. The Effect of Heat Treatment on Coating Thickness

Sectioned pieces of the molybdenum-iridium diffusion couples, measuring approximately 1/8-inch or 1/4-inch square, were metallographically polished on one side exposing both the molybdenum and the iridium. The thickness of iridium in the polished hot-pressed samples was measured by means of a microscope with a calibrated eye piece, and the average deviation of the measured iridium thickness for each of the samples was between one and two microns. As mentioned before, no reaction zone was observed in the 'as hot-pressed couples.' After vacuum annealing in the heat-treating apparatus previously described[2], the specimens were repolished on the same surface and the measurement repeated to determine both the decrease in thickness of the iridium coating and the thickness of the reaction zone formed. The results are listed in Table II.

TABLE II

Heat Treatment of Iridium Coated Molybdenum

Sample Number	Heat Treatment	Reaction Zone Width, Microns	Decrease in Iridium Thickness, Microns
7M-2	4 hrs. @ 1300°C	6.7	2.4
7M-9	7.8 hrs. @ 1300°C	9.6	0.2
7M-1	16.4 hrs. @ 1300°C	11.7	10.7
7M-7	4 hrs. @ 1500°C	21.6	7.8
6M-6	16.3 hrs. @ 1500°C	24.6	13.1
7M-8	1 hr. @ 1700°C	18.0	8.7
7M-4	4 hrs. @ 1700°C	27.7	12.5
7M-5	8.3 hrs. @ 1700°C	33.3	14.5
7M-3	16.6 hrs. @ 1700°C	51.2	22.4
7M-10	4 hrs. @ 1900°C	36.0	15.3
7M-11	6 hrs. @ 1900°C	46.2	27.2

The average deviation in the measurement of the thickness of iridium remaining after annealing varied between one micron and four microns. The magnitude of this average deviation is thought to depend largely upon (1) the amount of irregularity of the interface between the iridium and the iridium-rich intermetallic phase,(2) the difficulty in sharply resolving this interface microscopically due to a lack of contrast between the two adjacent phases,and (3) the surfaces of the sheets of iridium and molybdenum are neither optically flat nor perfectly parallel. Even though extreme care is taken to remove as little material as possible in repolishing the annealed specimens, the as-received iridium varied in thickness sufficiently to introduce errors of a few microns. Referring to the samples in Table II heat-treated at 1300°C,it can be seen that the reaction zone increases in width with increasing time and temperature. However, the calculated decrease in thickness of iridium is less for sample 7M-9 than for 7M-2 although 7M-9 was held at 1300°C almost twice as long as 7M-2. The growth of the reaction zone is independent of irregularities in thickness of the as-received iridium sheet; the calculated change in thickness of the iridium coating is directly related to these irregularities.

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REFERENCES

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2. Criscione, J.M., Volk, H.F., Mercuri, R.A., Nuss, J.W., Rexer, J., and Sarian, S., "High Temperature Protective Coatings for Graphite" under Contract AF33(657)-11253.

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